

NASA TECHNICAL NOTE



NASA TN D-2568

OK

AMPTIAC 58311

DISTRIBUTION STATEMENT A  
Approved for Public Release  
Distribution Unlimited

# ANOMALOUS ELECTRICAL RESISTIVITY OF PALLADIUM-DEUTERIUM SYSTEM BETWEEN 4.2° AND 300° K

by Robert J. Smith  
Lewis Research Center  
Cleveland, Ohio

Reproduced From  
Best Available Copy

---

**ANOMALOUS ELECTRICAL RESISTIVITY OF PALLADIUM-DEUTERIUM  
SYSTEM BETWEEN 4.2° AND 300° K**

By Robert J. Smith

Lewis Research Center  
Cleveland, Ohio

**20011130 139**

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**

---

For sale by the Office of Technical Services, Department of Commerce,  
Washington, D.C. 20230 -- Price \$1.00

# ANOMALOUS ELECTRICAL RESISTIVITY OF PALLADIUM-DEUTERIUM

SYSTEM BETWEEN  $4.2^{\circ}$  and  $300^{\circ}$  K

by Robert J. Smith

Lewis Research Center

## SUMMARY

The electrical-resistivity data of the palladium-deuterium (Pd-D) system with an atom ratio  $D/Pd$  of approximately 0.65 contain a peak near  $40^{\circ}$  K. This peak is similar to that obtained for the palladium-hydrogen (Pd-H) system and is accounted for by octahedral-tetrahedral transitions of some of the deuterium ions in the face-centered cubic lattice of palladium. Also, the resistivity is proportional to the temperature between  $110^{\circ}$  K and room temperature, as might be expected for palladium with a filled d-band; however, this relation is nonlinear for the Pd-H system, which indicates a broader temperature range for octahedral-tetrahedral transitions by hydrogen ions.

and

## INTRODUCTION

Start 1 Palladium (Pd) can easily absorb deuterium (D) or hydrogen (H) to an atom ratio  $D/Pd$  or  $H/Pd$  of 0.6. Normally, palladium has a 0.6 hole in its 4d-band, and it is assumed that the electron from the deuterium or hydrogen atom becomes associated with the 4d-band of palladium in such a way that when the atom ratio of 0.6 is obtained the d-band of palladium is completely filled. If the d-band were filled, the resistivity  $\rho$  would be proportional to the temperature  $T$  from approximately one-half the Debye temperature  $\Theta_D$  to near the melting point (ref. 1). For pure palladium, where the d-band is not filled, the curve of  $\rho$  as a function of  $T$  is concave toward the temperature axis from about  $70^{\circ}$  to at least  $700^{\circ}$  K ( $\Theta_{D,Pd} = 270^{\circ}$  K) (refs. 2 and 3). However, the curve of  $\rho$  as a function of  $T$  for an atom ratio  $H/Pd$  of 0.6 is concave away from the temperature axis up to at least  $250^{\circ}$  K (ref. 4 and fig. 1). In addition to this result, a pronounced peak in the resistivity curve occurred near  $43^{\circ}$  K. There was no explanation for this behavior at that time. It was believed that the nonlinearity in the resistivity curve up to  $250^{\circ}$  K and the peak at  $43^{\circ}$  K were both related to some ordering phenomenon.

To investigate this possibility, two experimental approaches were used. First, neutron-diffraction experiments were done on the Pd-H system in the temperature region of the peak. Second, resistivity experiments were done on the Pd-D system. Since atomic migration was required, resistivity measure- 2

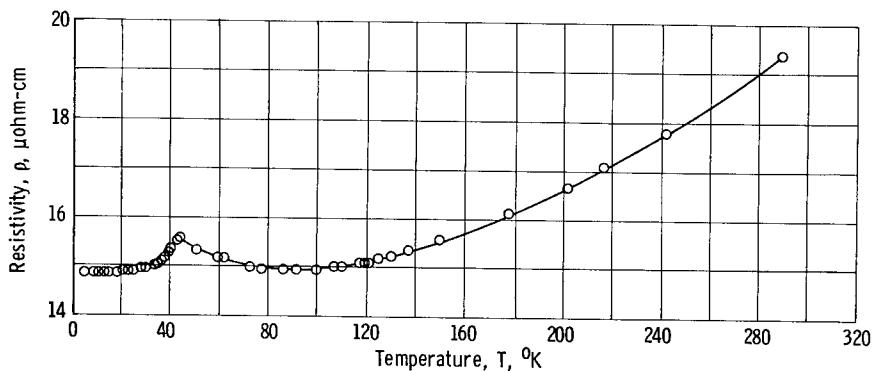


Figure 1. - Resistivity as function of temperature for palladium after absorption of hydrogen to hydrogen-palladium atom ratio of 0.6.

ments were expected to give somewhat different results because of the difference in mass and the possible difference in mobility, even though the systems should be identical electronically. The resistivity experiments were done at the Lewis Research Center and are reported herein; the neutron-diffraction work was done at the Naval Research Laboratory by Ferguson and Schindler and is reported in reference 5.

The neutron-diffraction work on the Pd-H system gave a reasonable explanation for the peak in the curve of resistivity as a function of temperature for the Pd-H system. Some of the hydrogen ions were found to occupy the tetrahedral interstitial sites at 77° K, whereas they occupy the octahedral or cube edge interstitial sites at room temperature. Ferguson and Schindler also did neutron-diffraction experiments on the Pd-D system. The results were erratic but, nevertheless, did indicate that some difference existed between the Pd-D and Pd-H systems at approximately 77° K. The determination of the resistivity as a function of temperature for the Pd-D system was therefore continued in order to help resolve these difficulties; the results are reported herein.

*back to 1*

#### EXPERIMENTAL PROCEDURE

The specimens used for the electrical-resistivity measurements were two lengths cut from 0.0385-centimeter-diameter palladium wire having a stated purity of 99.995 atomic percent palladium. One specimen was annealed at 800° C in a vacuum of  $10^{-6}$  millimeter of mercury for 1/2 hour, and the other was left in the unannealed or as-received state. For the resistance measurements, the length between the potential leads was 19.38 centimeters for the annealed specimen and 19.83 centimeters for the unannealed specimen. The resistance measurements were made with a double-ratio set and a standard resistor, which could be varied by powers of 10 from 100 down to  $10^{-4}$  ohm. The effect of resistance and thermal electromotive forces in the measuring leads of the specimen and the standard resistor were nullified in the double-ratio set. The double-ratio set can read to 1111.1 ohms in steps of 0.01 ohm, its limit of error being 0.01 percent at settings over 100 ohms. The accuracy of the standard resistor is 0.01 percent of the indicated value. A photocell-galvanometer amplifier system was

employed as the null device. Gold-2.1-atomic-percent-cobalt - copper thermocouples were used for temperature detection from 300° down to 20° K. From 20° to 1.5° K a germanium semiconductor probe was used. The thermocouples may be used down to 2° K, but their output is only 2.04 microvolts per °K at this temperature. The germanium probe has a reproducibility better than 0.05 percent of the temperature after cycling.

The absorption of the deuterium into the palladium was done electrolytically in a 0.1-normal deuterium sulfate - deuterium oxide solution with platinum as the anode and the palladium wire specimens as the cathode. The solution was mixed in a dry atmosphere, but the charging was done under normal room conditions. By use of a mass spectrometer, it was found that the gas constituents in sections of the specimens were 95 percent deuterium, and the remaining 5 percent was mostly hydrogen. The atom ratio D/Pd obtained by this process was determined from resistance measurements by using plots of  $R/R_0$  against deuterium content in palladium (data from ref. 6), where  $R_0$  is the initial resistance at 25° C prior to deuterium absorption, and  $R$  is the resistance value of a given concentration at 25° C. When the value of  $R/R_0$  indicated an atom ratio D/Pd greater than 0.6, the specimens were removed from the solution and immersed in liquid nitrogen. Resistance measurements were then made between 4.2° and 300° K.

## RESULTS

Prior to the absorption of deuterium by palladium, resistivity measurements were made on both the annealed palladium and the unannealed palladium wires at 4.2°, 77°, and approximately 300° K. After the absorption of deuterium to an atom ratio D/Pd greater than 0.6, resistivity data were obtained between 4.2° and 300° K. These results are shown in figure 2(a) for annealed palladium and absorbed deuterium and in figure 2(b) for unannealed palladium and absorbed deuterium. Above 110° K, the curves of  $\rho$  as a function of  $T$  are essentially linear up to 280° K. The curvature above 280° K indicates desorption of deuterium. Below 110° K both curves go through a minimum value in resistivity near 75° K. Both curves show a peak near 45° K; this peak is very well defined for unannealed palladium and absorbed deuterium. It should be mentioned that the temperature at which the peak occurs in the Pd-D system may be in error by a few degrees, since equilibrium data were not obtained over the dotted portion of the curve (fig. 2(b)).

Between 45° and 77° K it was necessary to allow the system to reach equilibrium, since the resistivity increased with time when the temperature was held constant ( $\pm 0.25$ ° K). The time needed for equilibrium varied from several minutes to 4 hours, depending on the temperature difference between successive measurements. The resistivity increased as much as 0.037 ohm-centimeter or 0.25 percent during the equilibration periods. (The rate of change of resistivity at constant temperature for the unannealed specimen was three times as fast as that for the annealed specimen.)

## DISCUSSION

Two temperature regions are considered for the curves of  $\rho$  as a function of  $T$  for the Pd-D system: (1) the region between  $110^{\circ}$  and  $300^{\circ}$  K, the linear portion, and (2) the region below  $110^{\circ}$  K, the portion involving the peak in the resistivity.

Between  $110^{\circ}$  and  $300^{\circ}$  K, the resistivity-temperature relation for the Pd-D system (fig. 2) is linear, whereas the normal resistivity-temperature relation for palladium is concave toward the temperature axis in this same region and is said to be caused by the decrease in the probability of s-d scatter with increasing temperature (ref. 7). For metals such as copper, silver, and gold, which have filled d-bands, the curves of  $\rho$  as a function of  $T$  are linear from at least  $\theta_D/2$  to near their melting points. Since the atom ratio  $D/Pd$  is greater than 0.6 in this experiment, it is assumed that the 4d-band of palladium is filled, and therefore that the s-d scatter probability is reduced to zero and that the resulting relation between  $\rho$  and  $T$  is linear. The

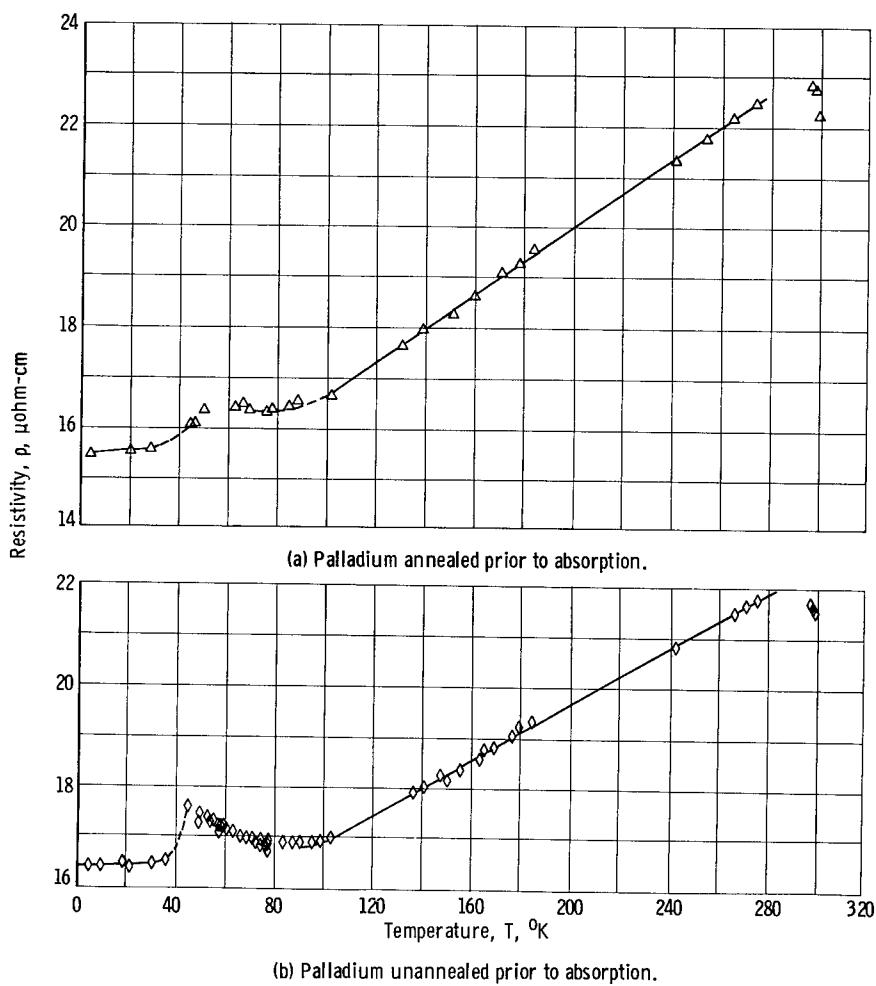


Figure 2. - Resistivity as function of temperature of palladium after absorption of deuterium to deuterium-palladium atom ratio greater than 0.6.

Debye temperature equivalent  $\theta_R$ , as calculated from the present data for the Pd-D system, is approximately  $220^\circ$  K and is within the linear portion of the resistivity-temperature curve.

A second point of interest in the curves of  $\rho$  as a function of  $T$  for the Pd-D system is the occurrence of a peak near  $45^\circ$  K. A reasonable explanation of this phenomenon is based on the following considerations. It has been shown that in the  $\beta$  phase (the normal room-temperature phase) of palladium the octahedral sites ( $1/2, 0, 0$ ;  $0, 1/2, 0$ ;  $0, 0, 1/2$ ; etc.) of the face-centered cubic lattice are occupied by the hydrogen or deuterium ions, and the lattice constant of the palladium atoms is approximately 4.02 angstroms (ref. 8). In the face-centered cubic lattice, another interstitial site is along the body, diagonal at the  $1/4, 1/4, 1/4$  or tetrahedral position. Ferguson and Schindler found these tetrahedral sites to be occupied to some extent by the hydrogen ions at  $77^\circ$  K. The number of ions in these sites was found to increase as the temperature was lowered from  $77^\circ$  K. The neutron-diffraction results for the Pd-D system were difficult to interpret, although a similar change was indicated in this system. The phase resulting from the occupation of the tetrahedral sites by the hydrogen or deuterium ions is referred to herein as  $\beta^*$  palladium to differentiate this configuration from the normal  $\beta$  palladium found at room temperature. It should be pointed out that no dimensional change of the expanded face-centered cubic palladium lattice was found in either the Pd-H or the Pd-D system during the transitions from  $\beta$  to  $\beta^*$ .

Since the ratio  $\beta^*/\beta$  increases with decreasing temperature, it is reasonable to suggest that the maximum in the curves of  $\rho$  as a function of  $T$  for the Pd-D and Pd-H systems below  $110^\circ$  K is due to the gradual mixing of  $\beta$  and  $\beta^*$  palladium; this mixing gives a higher resistivity than that for either phase alone and is similar to the mixing of noble metals at constant temperature, as shown in figure 3. Some insight into why this transition occurs may be gained by consideration of the slope of the curve of  $\rho$  as a function of  $T$

for pure palladium over the temperature range used for the Pd-H and Pd-D experiments. The resistivity is proportional to the square of the atomic displacement from at least  $\theta_D/2$  to near the melting point for several metals. (It has been found that this lower limit may extend down to  $0.2 \theta_D$ .) For pure palladium this relation is modified because of the s-d scatter of the conduction electrons. In any case, changes in the crystal lattice vibrations do affect  $d\rho/dT$ . Rather extreme changes in  $d\rho/dT$  for pure palladium occur at  $40^\circ$  and  $75^\circ$  K and are shown in figure 4, a plot of  $\frac{d}{dT} \left( \frac{d\rho}{dT} \right)$  against  $T$ . For the Pd-D and Pd-H systems, it is noted that the minimum in the curves of  $\rho$  as a function of  $T$  occurs near  $75^\circ$  K (where transitions from  $\beta$  to  $\beta^*$  start to dominate the resistivity); also, the peaks in these curves are near  $40^\circ$  K. While the detailed mechanisms of the transition are not apparent, it

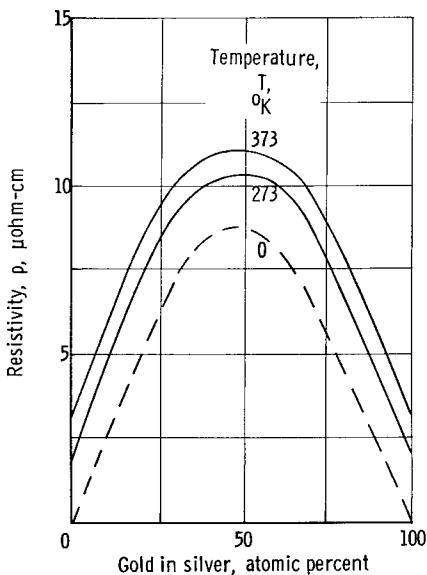


Figure 3. - Mixing of gold and silver at constant temperature.

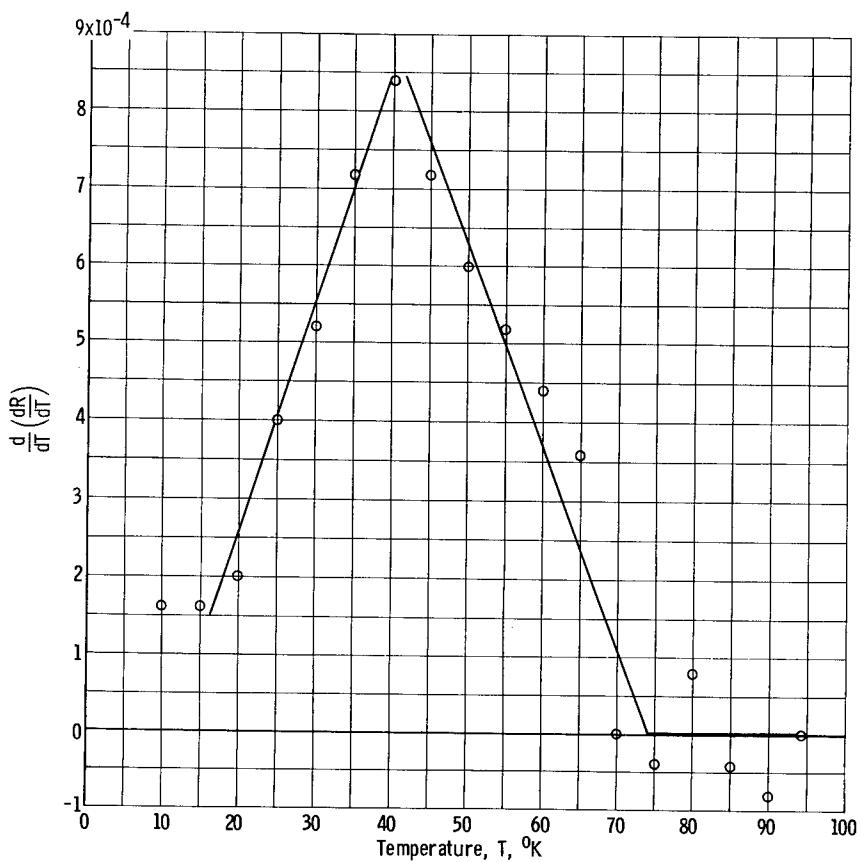


Figure 4. - Change in slope of curve of resistivity as function of temperature for annealed palladium plotted against temperature. Error in data is no greater than  $\pm 0.4$  in  $d^2T(dR/dT)$  above  $50^{\circ}$  K and less than  $\pm 0.4$  below  $50^{\circ}$  K; extreme changes occur near  $40^{\circ}$  and  $75^{\circ}$  K.

is reasonable to expect that the change in lattice dynamics of the palladium atoms is responsible for the octahedral-tetrahedral transitions of the deuterium or hydrogen ions. The occurrence of the peaks for both the Pd-D and Pd-H systems at the same temperature tends to support the idea that a property of the host palladium lattice is involved.

While the Pd-D and Pd-H systems are alike in some aspects, there are, however, some dissimilarities that are apparently due to the mass difference between the hydrogen and deuterium ions. No linear relation exists between  $\rho$  and  $T$  for the Pd-H system (fig. 1) in the temperature region studied, but  $\rho$  is proportional to  $T$  from  $110^{\circ}$  to  $270^{\circ}$  K for the Pd-D system. This may result from a temperature-dependent mixed-phase region of  $\beta$  and  $\beta^*$  palladium that is broader for the Pd-H system than for the Pd-D system. This conclusion is not in conflict with the assumption that a filled d-band for palladium should result in a linear relation between  $\rho$  and  $T$ , since that assumption is based on a lattice configuration that is constant with temperature. The most marked contrast between the Pd-H and Pd-D systems appears in the time dependence of the resistivity at constant temperatures between  $90^{\circ}$  and  $40^{\circ}$  K. For the Pd-D system, periods of up to 4 hours were recorded before the system reached equilibrium. No such time dependence was found for the Pd-H system. This time dependence could be responsible for the problems that arose in the

interpretation of the neutron-diffraction data for the Pd-D system. Since neutron-diffraction experiments depend on steady-state conditions and take several hours to complete, it seems that, if meaningful results are to be obtained for the Pd-D system below 110° K, the system should be kept at the experimental temperature at least 4 hours prior to starting the diffraction experiments so that the  $\beta$  and  $\beta^*$  phases can reach equilibrium.

Lewis Research Center  
National Aeronautics and Space Administration  
Cleveland, Ohio, October 12, 1964

#### REFERENCES

1. Gerritsen, A. N.: Metallic Conductivity. Vol. XIX of Handbuch der Physik, S. Flügge, ed., Springer Verlag (Berlin), 1956, p. 161.
2. Smith, R. J., Schindler, A. I., and Kammer, E. W.: Electric Resistivity and Thermoelectric Power of Palladium After Hydrogen Desorption. Phys. Rev., vol. 127, no. 1, July 1, 1962, pp. 179-183.
3. Schindler, A. I., Smith, R. K., and Salkovitz, E. I.: Electrical Resistivity of the Ni-Pd Alloy System Between 300° K and 730° K. Phys. Rev., vol. 108, no. 4, Nov. 15, 1957, pp. 921-923.
4. Schindler, A. I., Smith, R. J., and Kammer, E. W.: Low Temperature Dependence of the Electrical Resistivity and Thermoelectric Power of Palladium and Palladium-Nickel Alloys Containing Absorbed Hydrogen. Proc. Tenth Int. Cong. on Refrigeration, Copenhagen (Denmark), 1959, Vol. 1, Pergamon Press, 1960, pp. 74-79.
5. Ferguson, G. A., and Schindler, A. I.: Reports of NRL Progress, April 1962. Naval Res. Lab., Apr. 1962, p. 42.
6. Sieverts, A., and Danz, W.: The Electrical Resistance and Magnetic Susceptibility of Palladium Wire Charged with Deuterium. Zs. Phys. Chem., vol. 38B, 1937, pp. 61-71.
7. Mott, N. F., and Jones, H.: The Theory of Properties of Metals and Alloys. Clarendon Press (Oxford), May 1936, p. 244.
8. Worsham, J. R., Jr., Wilkinson, M. K., and Shull, C. G.: Neutron-Diffraction Observations on the Palladium-Hydrogen and Palladium-Deuterium Systems. Jour. Phys. Chem. of Solids, vol. 3, 1957, pp. 303-310.